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<p style="text-align: center;">Certificate of Mailing</p> <p>Date of Deposit <u>April 18 2001</u></p> <p>I hereby certify under 37 C.F.R. § 1.10 that this correspondence is being deposited with the United States Postal Service as "Express Mail Post Office to Addressee" with sufficient postage on the date indicated above and is addressed to BOX PCT, Assistant Commissioner for Patents, Washington, D.C. 20231.</p> <p>Guy E. Beardsley Printed name of person mailing correspondence</p> <p><i>Guy E. Beardsley</i> Signature of person mailing correspondence</p>		
Substitute Form PTO 1390 U.S. Department of Commerce Patent and Trademark Office <b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>		Attorney's Docket Number: 00246/514003 U.S. Application Number: Not Yet Assigned
INTERNATIONAL APPLICATION NUMBER	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/US99/24533	October 20, 1999	October 21, 1998
TITLE OF INVENTION:	LIQUID COMPOUNDS FOR FORMATION OF MATERIALS CONTAINING ALKALINE EARTH METALS	
APPLICANTS FOR DO/EO/US:	Roy G. Gordon and Daniel Teff	
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:		
1.	<input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. § 371.	
2.	<input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. § 371.	
3.	<input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. § 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. § 371(b) and PCT Articles 22 and 39(1).	
4.	<input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19 <sup>th</sup> month from the earliest claimed priority date.	
5.	A copy of the International Application as filed (35 U.S.C. § 371(c)(2)). <input type="checkbox"/> a. is transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> b. has been transmitted by the International Bureau. <input checked="" type="checkbox"/> c. Is not required, as the application was filed with the United States Receiving Office (RO/US).	
6.	<input type="checkbox"/> A translation of the International Application into English (35 U.S.C. § 371(c)(2)).	
7.	Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. § 371(c)(3)). <input type="checkbox"/> a. are transmitted herewith (required only if not transmitted by the International Bureau). <input type="checkbox"/> b. have been transmitted by the International Bureau. <input type="checkbox"/> c. have not been made; however, the time limit for making such amendments has NOT expired. <input checked="" type="checkbox"/> d. have not been made and will not be made.	
8.	<input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. § 371(c)(3)).	
9.	<input checked="" type="checkbox"/> An oath or declaration of the inventors (35 U.S.C. § 371(c)(4)).	
10.	<input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. § 371(c)(5)).	
11.	<input type="checkbox"/> An Information Disclosure Statement under 37 C.F.R. §§ 1.97 and 1.98.	
12.	<input type="checkbox"/> An assignment for recording. A separate cover sheet in compliance with 37 §§ 3.28 and 3.31 is included.	
13.	<input type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment.	
14.	<input type="checkbox"/> A substitute specification.	
15.	<input type="checkbox"/> A change of power of attorney and/or address letter.	
16.	<input checked="" type="checkbox"/> Other items or information: postcard, check	

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17.	■ The following fees are submitted:			
	BASIC NATIONAL FEE (37 C.F.R. § 1.492(A)(1)-(5)):			
	Neither international preliminary examination fee (37 C.F.R. § 1.482) nor international search fee (37 C.F.R. § 1.455(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO			\$ 1000.00
	International preliminary examination fee (37 C.F.R. § 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO			\$ 860.00
	International preliminary examination fee (37 C.F.R. § 1.482) not paid to USPTO but international search fee (37 C.F.R. § 1.445(a)(2)) paid to USPTO			\$ 710.00
	International preliminary examination fee (37 C.F.R. § 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1) - (4)			\$ 690.00
International preliminary examination fee paid to USPTO (37 C.F.R. § 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)			\$ 100.00	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$ 710.00
Surcharge of \$130 for furnishing the oath or declaration later than <input type="checkbox"/> 20 OR <input type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. § 1.492(e)).				\$ 0
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	23- 20 =	3	x \$18	\$ 54.00
Independent claims	3 - 3 =	0	x \$80	\$ 0
Multiple dependent claims (if applicable)			+ \$270	\$ 270.00
TOTAL OF ABOVE CALCULATIONS =				\$ 1034.00
Reduction of 1/2 for filing by small entity, if applicable. Applicant claims small entity status under 37 C.F.R. § 1.27				\$ 517.00
SUBTOTAL =				\$ 517.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 OR <input type="checkbox"/> 30 months from the earliest claimed priority date (37 C.F.R. § 1.492(f)). +				\$ 0
TOTAL NATIONAL FEE =				\$ 517.00
Fee for recording the enclosed assignment (37 C.F.R. 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. §§ 3.28, 3.31). +				\$ 0
TOTAL FEES ENCLOSED =				\$ 517.00
			Amount to be refunded	\$
			charged	\$
<ul style="list-style-type: none"> <li>■ a. A check in the amount of \$517.00 to cover the above fees is enclosed.</li> <li>■ b. Please charge my Deposit Account No. 03-2095 in the amount of \$ [**.**] to cover the above fees.</li> <li>■ c. The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment, to Deposit Account No. 03-2095.</li> </ul>				
NOTE: Where an appropriate time limit under 37 C.F.R. §§ 1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. § 1.137(a) or (b) must be filed and granted to restore the application to pending status.				
SEND ALL CORRESPONDENCE TO:		 Signature Susan M. Michaud Kristina Bieker-Brady, Ph.D. Clark & Elbing LLP 176 Federal Street Boston, MA 02110-2214 Telephone: 617-428-0200 Facsimile: 617-428-7045 Kristina Bieker-Brady, Ph.D. Reg No. 39,109 Reg. No. 42,885		

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Revised: 17 March 2000

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PATENT TRADEMARK OFFICE

LIQUID COMPOUNDS FOR FORMATION OF  
MATERIALS CONTAINING ALKALINE EARTH METALS

This invention was made with the support of the United States government under National Science Foundation Grant No. NSF CHE-95-10245. The United States may have certain rights in the invention.

Background of the Invention

1. Field of the Invention

This invention relates to novel volatile liquid reagents which can replace less satisfactory solid sources in film deposition processes such as chemical vapor deposition (CVD), spray coating, spin coating or sol-gel deposition. These liquid reagents can be used for deposition of materials containing alkaline earth metals, such as metal oxides or mixed metal oxides.

2. Description of the Related Art

Chemical vapor deposition (CVD) is a widely-used process for forming solid materials, such as coatings or powders, from reactants in the vapor phase.

15 Comprehensive reviews of CVD processes have been given recently in "CVD of Nonmetals," W. S. Rees, Jr., Editor, VCH Publishers, Weinheim, Germany, 1996; "CVD of Compound Semiconductors," A. C. Jones and P. O'Brien, VCH, 1996; and "The Chemistry of Metal CVD," T. Kodas and M. Hampden-Smith, Editors, VCH, 1994.

20 In CVD processes, a reactant vapor may be created by heating a liquid to a sufficiently high temperature and bubbling a flow of a carrier gas through the liquid, to transport the vapor into the CVD chamber. In a low-pressure CVD system, the carrier gas may be omitted, and the vapor may flow directly from the bubbler into the low-pressure CVD chamber.

25 In order for a CVD process to function successfully, it is necessary to create a vapor containing controlled amounts of suitably reactive chemicals. Solids can be

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used as sources of vapor in CVD processes. However, when solids are used in a bubbler, the rate of vapor production by sublimation of a solid is not easily reproducible, because the amount of vapor produced often depends on the particle size and shape, which change as the sublimation process continues. Thus the vapor concentration can change in an uncontrolled way, thereby changing the growth rate and/or the composition of materials made by the CVD process. Also, different batches of solid may have different sizes and shapes of particles, so that the results of a CVD process may change when a new batch of solid precursor is placed in the system.

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These difficulties are particularly evident in the currently-used CVD precursors for barium, strontium and calcium, which are reviewed by W. A. Wojtczak, P. F. Fleig and M. J. Hampden-Smith, in *Advances in Organometallic Chemistry*, vol. 40, pp. 215-340 (1996).

Another problem with solids is that their rate of sublimation can be altered by small amounts of contamination on their surfaces. In contrast, liquid surfaces tend to be refreshed by motion of the liquid, so that they tend to evaporate at a reproducible rate even in the presence of small amounts of contaminants.

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Some solid materials show different vapor pressures, depending on the history of how the particular sample was prepared or how long it has been stored. For example, barium 2,2,6,6-tetramethyl-3,5-heptanedionate, often abbreviated as Ba(thd)<sub>2</sub>, has been used to deposit barium strontium titanate (BST) films. Solid Ba(thd)<sub>2</sub> exists in a number of oligomeric forms, ranging from trimers to tetramers to polymers of various lengths, depending on the method used for its synthesis. The rates of interconversion between oligomeric forms are slow, often taking weeks or months. Thus the molecular composition of a sample of Ba(thd)<sub>2</sub> depends on how it was made and how long it has been stored. The vapor pressures of these oligomers are different from each other. Thus it is very difficult to predict the vapor pressure of any particular sample of Ba(thd)<sub>2</sub> and the deposition rate of BST from this solid source is not reproducible. In comparison, liquids usually exist in only one reproducible form at any given temperature and pressure.

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Another difficulty with solids is that rates of sublimation are often low, so that sufficiently high vapor concentrations cannot be produced. For example, Ba(thd)<sub>2</sub> has a very low vapor pressure, which limits the deposition rate to low values. In comparison, liquids often have higher vapor pressures than solids.

5 Another practical difficulty with solids is that transferring them between containers is less convenient than pumping liquids.

Thermal decomposition of solids is another problem that often affects the reproducibility of solid vapor sources. For example, the solid beta-diketonates of barium, such as Ba(thd)<sub>2</sub>, gradually decompose at their vaporization temperatures, so that the amount of vapor generated decreases with time. Thermal decomposition is also a potential problem for liquid sources, but its effect may be minimized for liquids by rapid or "flash" vaporization. This can be accomplished by pumping the liquid at a steady, controlled rate into a hot region in which the liquid vaporizes quickly. In such a "direct liquid injection" (DLI) system, each part of the liquid is heated for only a short time, and its vapor can be formed without significant decomposition even from thermally sensitive liquids. Another advantage of a DLI system is that multicomponent mixtures can be vaporized in a fixed and reproducible ratio, even if the components differ in volatility. Because of these advantages, DLI systems are becoming more widely used in CVD processes.

20 Solid sources can be used in DLI vapor sources if a suitable liquid solvent can be found to dissolve the solid. However, solvents can introduce other difficulties, such as increased flammability, toxicity or corrosiveness of the precursor solution, increased incorporation of carbon or other impurities into the deposited film, and an increased volume of gaseous byproducts which must be removed from the exhaust gases to avoid pollution. These difficulties with a solvent can be minimized if the solid is highly soluble in the solvent, so that only a small amount of solvent is needed 25 to form the liquid solution.

Because of all these difficulties, solid sources of vapor are seldom used in commercial CVD processes. Either liquids, or solids that are highly soluble in a liquid

solvent, are more convenient, and more commonly used in the practice of CVD. Creating this vapor from a liquid source would be much more reproducible and convenient than creating it from a solid source; however, there are no previously known liquid compounds of barium, strontium, calcium or magnesium that may be used for this purpose.

The vapor pressures of beta-diketonates of alkaline earth metals may be increased by vaporizing them in the presence of amines (Gordon et al., U.S. Patent 5,139,999, 1992), ethers (Miller et al., U.S. Patent 4,501,602, 1985; Timmer et al., U.S. Patent 5,248,787, 1993; Kirlin et al., U.S. Patent 5,280,012, 1994) or thioethers (Kirlin et al., U.S. Patent 5,225,561, 1993). However, even when bound to these Lewis bases, the alkaline earth metal beta-diketonates disclosed in these references are still solids at room temperature.

Liquid precursors for many metals, including alkaline earth metals, have been successfully formed by using a mixture of several beta-diketonate ligands (Gordon et al, Materials Research Society Symposium, Vol. 495, pages 63-67, 1998). However, because these liquid precursors are mixtures of many compounds, they are harder to purify and characterize than single compounds. For example, they cannot be purified by crystallization because on cooling they form a single glassy solid, rather than separating into pure single crystals. Although some impurities can be removed by distillation, high purity cannot be obtained by distillation in a narrow temperature range. Because different components of the mixture have different vapor pressures, the mixture distills over a range of temperatures. Another difficulty with the use of these liquid mixtures is that a constant vapor composition of such mixtures cannot be continuously delivered from a bubbler source, since the more volatile components will distill out first.

### Summary of the Invention

A principal feature of the present invention to provide chemical precursors that are pure liquid compounds at room temperature, and that may be used for the

deposition of materials containing alkaline earth metals, particularly barium, strontium, calcium and magnesium.

An additional feature of the present invention is to provide chemical precursors that are easily vaporized without decomposition, and that do not leave a nonvolatile residue during a process for the deposition of alkaline earth metal-containing materials.

A related feature of the present invention is a process for deposition of alkaline earth metal-containing materials from chemical compounds that are liquids at room temperature.

Another related feature is to deposit materials containing several metals by a chemical vapor deposition process in which all the reactants may be mixed homogeneously before delivery to the heated surface of the substrate.

An additional feature of the present invention is a process for the deposition of alkaline earth metal-containing materials from chemical precursors that are easily vaporized without decomposition, and that do not leave a nonvolatile residue.

Another feature of the present invention is to provide a process for making mixed metal oxides, including alkaline earth metal oxides, having high purity.

Another feature of the invention is to provide a chemical vapor deposition process for metal oxides from reactants that are stable and relatively nonhazardous.

Another feature of the invention is to provide a chemical vapor or solution deposition process for complex metal oxides in which the precursor metal-containing compounds are stable and homogeneous liquids.

A further feature of the invention is to provide liquid mixtures or solutions suitable for spray coating, spin coating or sol-gel deposition.

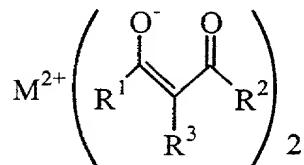
Another feature of the present invention is to provide a liquid precursor for use in forming titanium dioxide and other titanium-containing materials.

One particular feature of the present invention is to provide a process for depositing barium strontium titanate coatings having a high dielectric constant and a high electrical resistance.

Another particular feature of the present invention is to provide a process for depositing barium titanate having ferroelectric properties.

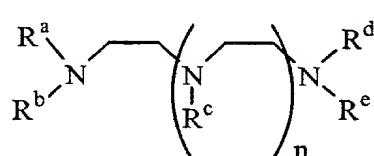
The above features have been substantially achieved by use of a composition comprising an alkaline earth metal beta-diketonate having one or more particular 5 amine ligands bound to the metal. In preferred embodiments, the compound is a liquid at 60 °C, and preferably at 20 °C, and is capable of being vaporized..

The alkaline earth metal beta-diketonate has the general formula,



where <sup>1</sup>R and R<sup>2</sup> may be an alkyl group, a fluoroalkyl group or an alkyl group containing oxygen- or nitrogen-containing species (for example, an amino, alcohol or alkoxy species). R<sup>3</sup> may be hydrogen or an alkyl group, a fluoroalkyl group or an alkyl group containing oxygen- or nitrogen-containing species. In preferred 15 embodiments, the alkyl groups contain less than ten carbons and preferably less than seven carbons. Preferred compositions of the alkaline earth metal diketonates includes 20 ligands derived from 2,2,6,6-tetramethyl-3,5-heptanedione, abbreviated as Hthd, 2,2,6,6-tetramethyl-3,5-octanedione, abbreviated as Htod, 3,3,7,7-tetramethyl-4,6-nonanedione, abbreviated as Htn, and 2,2,6-trimethylheptane-3,5-dione, abbreviated as H3hd, where the H indicates the presence of a hydrogen atom that is removed when the ligand is bound to an alkaline earth metal.

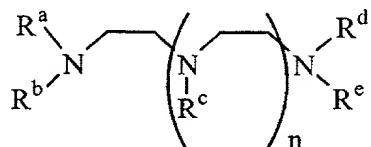
Preferred amines have the general formula:



in which n is a non-negative integer, and R<sup>a</sup>, R<sup>b</sup>, R<sup>c</sup>, R<sup>d</sup> and R<sup>e</sup> are hydrogen, an alkyl group or 30 a substituted alkyl group, such that n=0 corresponds to a diamine, n=1 corresponds to a

triamine and n=2 corresponds to a tetramine.

In another embodiment, preferred amines include N-substituted amines having the general formula:



in which n is a non-negative integer, preferably in the range of 0 to 3, and more preferably, 0, 1, 2, or 3, such that n=0 corresponds to a diamine, n=1 corresponds to a triamine and n=2 corresponds to a tetramine, and Ra, Rb, Rc, Rd and Re are independently selected and are hydrogen, an alkyl group, a substituted alkyl group or aryl group. Substituted alkyl groups include those substituents which have a minimal effect on volatility or melting point of the product alkaline earth metal beta-diketonate compound, and include, but are not limited to, fluoroalkyl groups, or an alkyl group containing an oxygen-containing species. Ra, Rb, Rc, Rd and Re are selected to provide a volatile complex with an alkaline earth metal beta-diketonate. One or more of the groups Ra, Rb, Rc, Rd and Re desirably is larger than a methyl group and the total number of carbon atoms on the amine is desirably in the range of 4 to 20. N-alkyl substituted polyamines with alkyl chain lengths from about 4 to 8 carbon atoms promote the formation of liquid adducts. The liquid viscosity decreases with increasing numbers of carbon atoms in the alkyl chains. In a preferred embodiment, the amine ligand is a triamine, such as N,N',N''-trihexyldiethylenetriamine.

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An amine adduct of an alkaline earth metal beta-diketonate is formed by reacting the alkaline earth metal beta-diketonate with an amine. In the case of a triamine, generally one equivalent of the triamine is used for one equivalent of an alkaline earth metal beta-diketonate. Two equivalents of a diamine may be reacted with one equivalent of a barium, strontium or calcium beta-diketonate, but only one diamine typically binds to a magnesium beta-diketonate.

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In the most preferred embodiments, the amine adduct of a metal beta-diketonate is a liquid at room temperature. It was discovered that N-alkyl substituted

polyamines with alkyl chain lengths from about 4 to 8 carbon atoms promote the formation of liquid adducts. The liquid viscosity decreases with increasing numbers of carbon atoms in the alkyl chains.

In another embodiment of the invention, the complexed alkaline earth metal beta-diketonate is a solid that is highly soluble in organic solvents. The metal beta-diketonate compound may preferably be prepared in concentrations of greater than 0.1 M, more preferably greater than 0.5 M and most preferably greater than 1.0 M.

In some cases, amine ligands with only two types of substituents may be sufficient to achieve the properties cited above. In other cases, three or four or even more different substituents on the amine ligands may be desired.

Another aspect of the invention provides a process for the chemical vapor deposition of materials comprising alkaline earth metals, using vapors from an amine-complexed alkaline earth metal beta-diketonate and, optionally, another oxygen-containing gas. The process may be used to form films, including, but not limited to, barium, strontium, calcium and magnesium. A preferred embodiment uses a homogeneous vapor mixture comprising an amine-complexed alkaline earth metal beta-diketonate, oxygen and, optionally, an inert carrier gas such as nitrogen. This vapor mixture is brought into contact with a substrate heated to a temperature sufficient to deposit a material comprising one or more alkaline earth metals. Typical deposition temperatures lie in the range of about 200 to 800 °C. Typical deposition pressures range from normal atmospheric pressure down to a few milli-Torr.

A preferred embodiment uses a homogenous liquid mixture of one or more amine-complexed metal beta-diketonates along with one or more other volatile metal-containing compounds. This liquid mixture is vaporized to form a vapor mixture and optionally mixed with an oxygen-containing gas, such as air, and an inert carrier gas such as nitrogen. This vapor mixture is heated to a temperature sufficient to cause reaction and the formation of a material comprising two or more metal oxides. Alternatively, reaction may be caused by light, or by the electrical energy of a plasma discharge.

In another embodiment of the invention, multimetal oxides are formed from solutions of one or more amine-complexed metal beta-diketonates along with one or more other volatile metal-containing compounds and a solvent, in deposition processes as described herein. The process may be used to form multimetal oxide films, 5 including, but not limited to, barium ferrites, barium titanate, strontium bismuth tantalate and barium strontium titanate.

The liquid amine-complexed metal beta-diketonates may also be used, neat or as highly concentrated solutions, in film deposition methods such as sol-gel formation, spray-coating or spin-coating. Aryl-containing amines and/or higher carbon-containing amines are well-suited for such applications, as the higher carbon-content of the alkyl or aryl groups may result in a compound having lower volatility than comparable compounds having alkyl-containing amines.

#### Brief Description of the Drawing

15 Figure 1 is an x-ray crystallographic structure of the compound of strontium bis(2,2,6,6-tetramethylheptane-3,5-dionate) with N,N',N"-triethylenetriamine, which can be abbreviated as Sr(thd)<sub>2</sub>·tadeta.

#### Detailed Description of the Invention

##### 20 1. Beta-Diketone Ligands

Table 1 gives the names of some beta-diketone ligands that are suitable for the practice of the invention. Table 1 also gives the numbers assigned by Chemical Abstracts to the compounds. The general formula may be written  $^1\text{RC}(=\text{O})\text{CHR}^3\text{C}(=\text{O})\text{R}^2$ , where  $^1\text{R}$  and  $\text{R}^2$  may be an alkyl group, a fluoroalkyl group 25 or an alkyl group containing oxygen- or nitrogen-containing species (for example, an amino, alcohol or alkoxy species).  $\text{R}^3$  may be hydrogen or an alkyl group, a fluoroalkyl group or an alkyl group containing oxygen- or nitrogen-containing species. In preferred embodiments, the alkyl groups contain less than ten carbons and preferably less than seven carbons.

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Table 1. Some preferred beta-diketone ligands

Chemical Name	Nickname	<sup>1</sup> R	<sup>2</sup> R	<sup>3</sup> R	t	CAS No.
2,2,6,6-tetramethylheptane-3,5-dione	Hthd	<sup>1</sup> Bu	<sup>1</sup> Bu	H	0	1118-71-4
2,2,6,6-tetramethyloctane-3,5-dione	Htod	<sup>1</sup> Bu	<sup>1</sup> Am	H	2	78579-61-0
3,3,7,7-tetramethylnonane-4,6-dione	Htnd	<sup>1</sup> Am	<sup>1</sup> Am	H	4	138024-17-6
2,2,6-trimethylheptane-3,5-dione	H3hd	<sup>1</sup> Bu	<sup>1</sup> Pr	H	1	7333-23-5

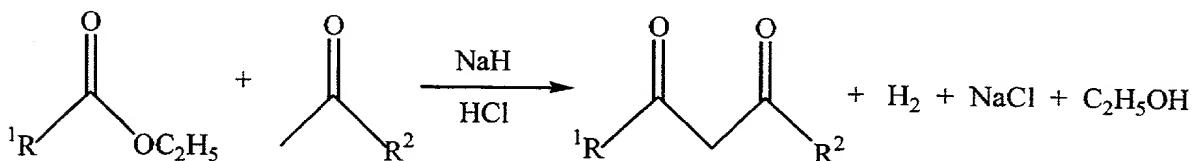
The number t in this table is the number of torsion angles corresponding to rotation around C-C single bonds. Rotation angles of methyl or tert-butyl groups about their three-fold axes were not counted, since these motions don't change the intermolecular interactions as much as the other torsions do. As t increases, the number configurations available to the ligand increases, and thus its ability to frustrate crystallization of its compounds. Thus the larger t is, the greater is the ability of the ligand to keep its compounds in liquid form.

Some or all of the oxygens in the beta-diketonate ligands may be replaced by isoelectronic species, such as sulfur or NH or NR, where R is a hydrocarbon radical. For the purposes of this specification and claims, these isoelectronically substituted beta-diketonate ligands shall be considered as beta-diketonate ligands.

Some or all of the hydrogens in the beta-diketonate ligands may be replaced by fluorine. Fluorine substitution may be used to deposit fluorides instead of oxides. Fluorine substitution may also provide higher vapor pressures of the precursor compounds.

## 2. Synthesis of Beta-Diketonate Ligands

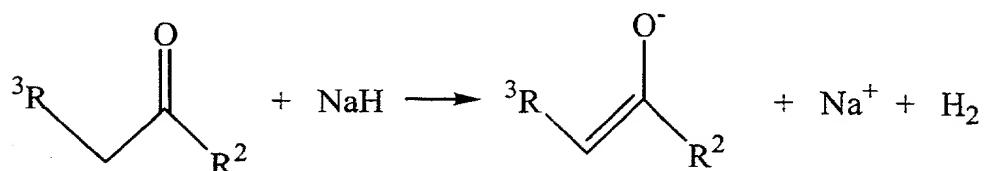
The required beta-diketone ligands may be prepared by known methods, such as the Claisen condensation of a methyl ketone and an ethyl ester, in the presence of a strong base, such as sodium hydride.



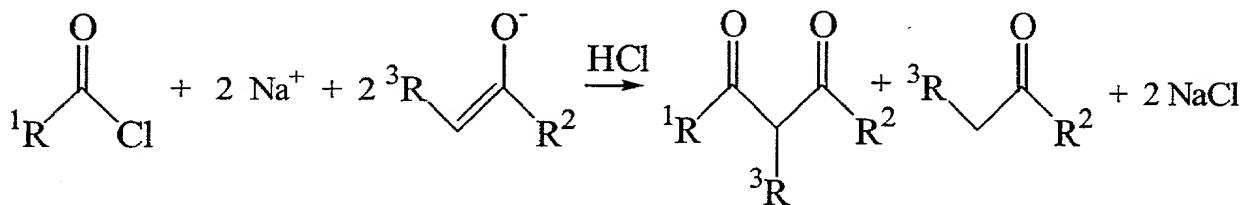
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A detailed description of this procedure is given in Inorganic Syntheses, Vol. 23, pp. 144-145 (1985).

5 A preferred way to synthesize these beta-diketone ligands is first to react an appropriate ketone with a strong base, such as sodium hydride, in the presence of a donor solvent, such as tetrahydrofuran (THF), to form a solution of the corresponding sodium enolate:



This enolate is then reacted with an appropriate organic acid chloride, neutralized with a mineral acid and filtered to remove the salt precipitate, to form the desired beta-



diketone:

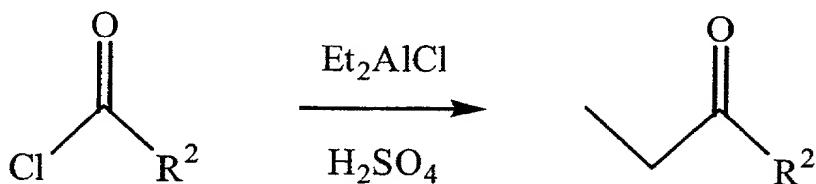
15 Distillation under low pressure then yields the desired beta-diketone in higher yield and better purity than the traditional Claisen condensation. The excess starting ketone can be recovered and reused for further syntheses. This method is particularly effective when the R<sup>2</sup> group is a tertiary alkyl group, such as tertiary butyl or tertiary amyl.

20 As a specific example of this method, the synthesis of the beta-diketone 2,2,6,6-tetramethyloctane-3,5-dione (Htod) is given as follows: All experimental manipulations were carried out under dry nitrogen either in a glovebox or on a Schlenk line unless otherwise stated. Sodium hydride (NaH) (14.23 g, 593 mmol) was suspended in 400 mL of dry tetrahydrofuran (THF) and heated to 85 °C. Pinacolone (70 ml, 560 mmol) was added at 4.4 mL/min, and vigorous bubbling of hydrogen (H<sub>2</sub>)

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gas began after the first 10 mL was added. The addition was continued at a rate of addition low enough to keep the reaction from bubbling too vigorously. After the addition was completed, the reaction was stirred at 85 °C until the bubbling stopped after about 10 min (i.e. when no more bubbles were observed passing through an oil bubbler which was vented to the atmosphere). The pale yellow suspension was then cooled to room temperature and filtered through celite to remove excess NaH. The clear, pale yellow filtrate was cooled to 0 °C and neat 2,2-dimethylbutyryl chloride (34.5 mL, 252 mmol) was added at 3.1 mL/min while stirring, giving a very turbid, light yellow suspension. This was removed from the ice bath and stirred for 15 min and again cooled to 0 °C. At this point, the mixture contained 0.25 eq. NaCl, 0.25 eq. pinacolone, 0.25 eq. Na(β-diketonate) and 0.05 eq. Na(enolate). Then 34 mL of concentrated aqueous HCl was added to give a fluffy, white solid precipitate of NaCl in a clear, colorless solution. MgSO<sub>4</sub> was added in an amount sufficient to absorb the water, the mixture was stirred for 30 min and then filtered. The solid was washed with 100 mL of hexanes, and the washings combined with the filtrate. Distillation was used to remove the solvents and excess pinacolone, leaving a pale yellow liquid (46.02 g, 92%) which was shown to be the desired product, 2,2,6,6-tetramethyloctane-3,5-dione (Htod), by NMR analysis. The product distilled at 147-150 °C at 149 mbar.

The other beta-diketones were made in a similar manner, by substituting other ketones for the pinacolone, and/or other acid chlorides for the 2,2-dimethylbutyryl chloride. For beta-diketones having R<sup>3</sup> = methyl, the required ethyl ketones are not commercially available. These ethyl ketones were synthesized by ethylation of appropriate commercially available acid chlorides with diethylaluminum chloride as the ethyl source, according to the general reaction:



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As a specific example of this method, tert-amyl ethyl ketone (4,4-dimethyl-3-hexanone) was made as follows: 21.3 ml 2,2-dimethylbutyryl chloride was mixed with 40 ml of dry and degassed dichloromethane,  $\text{CH}_2\text{Cl}_2$ , and the solution cooled to -30 °C. 19.18 g of diethylaluminum chloride,  $(\text{CH}_3\text{CH}_2)_2\text{AlCl}$ , dissolved in 40 ml of  $\text{CH}_2\text{Cl}_2$ , was added at about 1 drop per second while maintaining the temperature of the reaction mixture between -35 and -30 °C. The first few drops caused some smoke, but later the smoke disappeared. After complete addition, the liquid solution was warmed to 25 °C over a period of 1 hour, and stirred at 25 °C for an additional hour. Then the solution was slowly transferred by cannula to a rapidly-stirred mixture of 25 ml sulfuric acid,  $\text{H}_2\text{SO}_4$ , 25 ml of water and 250 g of ice. A white precipitate formed, along with some bubbling, and then the precipitate gradually dissolved. The organic layer was removed, and the aqueous layer was washed with dichloromethane, and the combined organic layer and washings were dried over magnesium sulfate,  $\text{MgSO}_4$ . The mixture was filtered and the solvent removed from the filtrate under reduced pressure, leaving 11.33g (57%) of a very pale yellow liquid. NMR confirmed that the product was 4,4-dimethyl-3-hexanone.

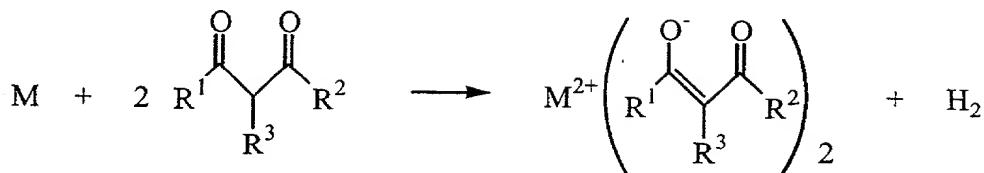
A commercial source was not found for tert-amyl methyl ketone, which is required to make some of the preferred beta-diketones. Tert-amyl methyl ketone can be synthesized by methylating 2,2-dimethylbutyryl chloride with methylaluminum sesquichloride,  $\text{Me}_3\text{Al}_2\text{Cl}_3$ , using a similar procedure to the one just described for 4,4-dimethyl-3-hexanone.

### 3. Synthesis of Alkaline Earth Beta-Diketonates

Compounds can be formed between these beta-diketonate ligands and most metals. Two ligands can be bound to metal ions in oxidation state +2, including beryllium, magnesium, calcium, strontium and barium. Many different reactions can be used to bind beta-diketonate ligands to metals. Specific examples of preparative procedures are given in Inorganic Syntheses, for beryllium in Vol. 2, pp. 17-20 (1946); and for calcium, strontium and barium in Vol. 31, pp. 1-7 (1997). In particular, the alkaline earth metal may be reacted with the beta-diketone ligand to form a metal beta-

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diketonate compound:



As a specific example of this method, there follows a preparation of barium 2,2,6,6-tetramethyl-3,5-octanedionate,  $\text{Ba}(\text{tod})_2$ . 1.29 g barium metal and 3.728 g 10 2,2,6,6-tetramethyl-3,5-octanedione (tod) were placed together in a flask and immediately bubbles of hydrogen began to form. 25 ml of benzene was added and the reaction appeared to slow. After bubbling ammonia gas through the mixture for 2 minutes, the bubbling became vigorous. After 30 minutes, the bubbling slowed, so ammonia was again bubbled for 5 minutes. This procedure was continued for 4 hours 15 until almost no metal remained. The pressure was reduced for a few minutes to remove dissolved ammonia. Then the mixture was filtered through celite, giving a clear, colorless solution. The benzene solvent was removed by evaporation under reduced pressure, yielding a 3.9 g (78%) of a glassy solid.

4. Amines

20 A variety of amines may be used in the practice of this invention. Polyamines with 2, 3 or 4 nitrogens are preferred, while triamines (3 nitrogens) are most preferred. Some specific preferred amines are listed in Table 2, which also gives the number assigned by Chemical Abstracts Service to those amines previously reported.

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Table 2. Some preferred amines of the general formula  $R^aR^bNCH_2CH_2(NR^aCH_2CH_2)_nNR^aR^b$ .

Name	Nickname	n	R <sup>a</sup>	R <sup>b</sup>	t	CAS No.
N,N',N"- triethyldiethylenetriamine	tedeta	1	Et	H	3	105-93-1
N,N',N"-triethyl-N,N"- dimethyldiethylenetriamine	tedmdeta	1	Et	Me	3	not reported
N,N,N',N",N"- pentaethyldiethylenetriamine	pedeta	1	Et	Et	5	24426-21-9
N,N',N"- tripropyldiethylenetriamine	tpdeta	1	Pr	H	6	175340-28-0
N,N'-dimethyl-N,N',N"- tripropyldiethylenetriamine	tpdmdeta	1	Pr	Me	6	not reported
N,N',N"- tributyl-diethylenetriamine	tbdeta	1	Bu	H	9	67708-18-3
N,N',N"-tributyl-N,N"- dimethyldiethylenetriamine	tbdmdeta	1	Bu	Me	9	not reported
N,N',N"- triamyldiethylenetriamine	tadeta	1	Am	H	12	not reported
N,N',N"-triaryl-N,N"- dimethyldiethylenetriamine	tadmdeta	1	Am	Me	12	not reported
N,N',N"- trihexyldiethylenetriamine	thdeta	1	He	H	15	not reported
N,N',N"-trihexyl-N,N"- dimethyldiethylenetriamine	thdmdeta	1	He	Me	15	not reported
N,N'-dibutylethylenediamine	dbeda	0	Bu	H	6	4013-95-0
N,N'-diamylethylenediamine	daeta	0	Am	H	8	88619-07-2

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5	N,N'-dihexylethylenediamine	dheda	0	Hex	H	10	57413-98-6
	N,N,N',N'-tetrabutylethylenediamine	tbeda	0	Bu	Bu	12	not reported
	N,N',N",N"-tetrabutyltriethylenetetramine	tbteta	2	Bu	H	12	not reported
	N,N',N",N"-tetraamyltriethylenetetramine	tateta	2	Am	H	16	not reported
	N,N',N",N",N"-pentapropyltetraethylenepentamine	pptepa	3	Pr	H	10	not reported
10	N,N',N",N",N"-pentabutyltetraethylenepentamine	pbtepa	3	Bu	H	15	not reported

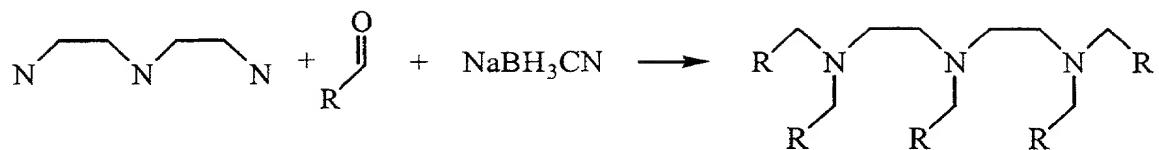
The number t in Table 2 is the number of angular variables (torsion angles corresponding to rotation around C-C single bonds). Angles that rotate methyl or tert-butyl groups about their three-fold axes were not counted, since these motions don't change the intermolecular interactions as much as the other torsion angles do.) As t increases, the number configurations available to the amine increases, and thus its ability to frustrate crystallization of amine adducts. Thus the larger t is, the greater is the ability of the amine to keep the adduct compound in liquid form and to lower the viscosity and the melting point.

Some or all of the hydrogens in the amine ligands may be replaced by fluorine. Fluorine substitution may be used to deposit fluorides instead of oxides. Fluorine substitution may also provide higher vapor pressures of the precursor compounds.

##### 5. Synthesis of Amines

The amines required in the practice of this invention can be synthesized by a number of methods. For the embodiments which use a polyamine in which all nitrogens are saturated with the same alkyl groups, it is convenient to use reductive alkylation with an aldehyde as the alkyl source and sodium cyanoborohydride as the reductant. For example, to fully alkylate a triamine, the general reaction may be

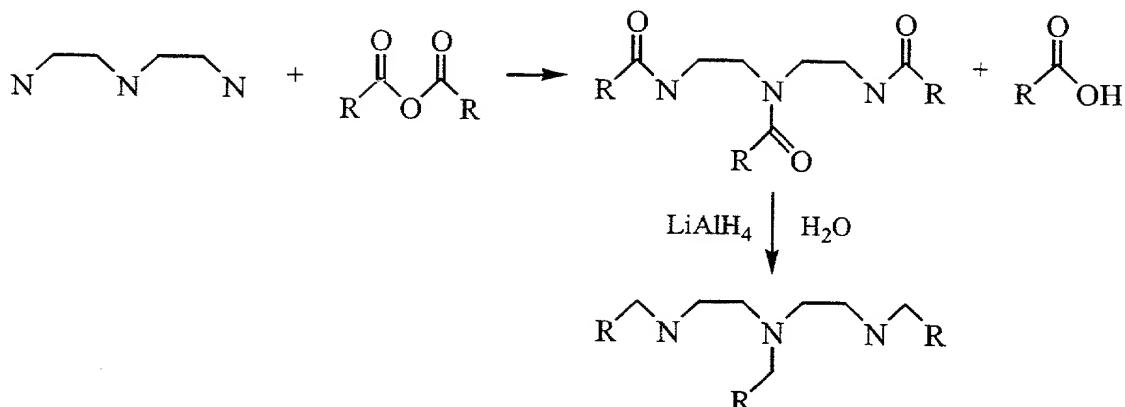
written as follows:



In one embodiment using this type of amine, the R groups in this formula are methyl groups. Thus the pendant groups on the nitrogens are ethyl groups, and this amine is called N,N,N',N",N"-pentaethyldiethylenetriamine, nicknamed pedeta. This material may be prepared by reacting diethylenetriamine,

10 H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, with acetaldehyde, CH<sub>3</sub>CHO, and sodium cyanoborohydride, NaBH<sub>3</sub>CN, in acetonitrile solution, following the procedure published for a similar reaction (R. F. Borch and A. I. Hassid, Journal of Organic Chemistry, volume 37, pages 1673-1674, 1972).

15 In other preferred embodiments, it is desirable to have two different groups attached to each terminal nitrogen. In this way more randomness and disorder is built into the molecules, further inhibiting crystallization and maintaining the disordered liquid state of the substance. A particularly desirable form of this embodiment combines a small group, such as hydrogen or a methyl group, on each terminal nitrogen with a second larger group, such as butyl, amyl (pentyl), or hexyl. The presence of the smaller group also minimizes the steric bulk of the ligand, and allows firm binding to the metal center. The synthesis of this type of polyamine can be carried out as follows. The commercially available unsubstituted polyamine is first acylated with an acid anhydride under conditions in which only one acyl group can attach to each nitrogen. Then the resulting polyamide is reduced with lithium 20 aluminum hydride:



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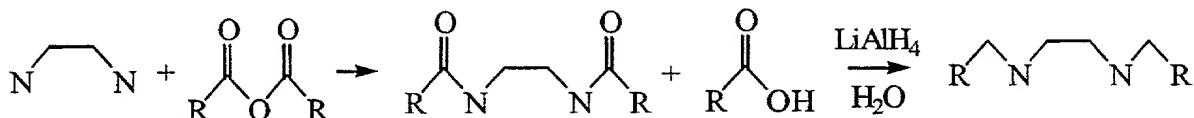
This procedure results in a polyamine in which the terminal nitrogens have one hydrogen (secondary amines) and the backbone nitrogen or nitrogens carry an alkyl group and no directly bonded hydrogen (tertiary amines). It is suitable for making amines such as N,N',N"-triethyldiethylenetriamine (tedeta), (CH<sub>3</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>CH<sub>3</sub>, N,N',N"-tripropylidethylenetriamine (tpdeta), (CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>, N,N',N"-tributylidethylenetriamine (tbdueta), (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NHCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, N,N',N"-triamyldiethylenetriamine (tadeta), (CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NHCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, and N,N',N"-trihexyldiethylenetriamine (thdueta), (CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>NHCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>N(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>.

Preparation of triethyldiethylenetriamine (tedeta) by this method is as follows: 10 ml diethylenetriamine, H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>NHCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, in 40 ml diethyl ether (Et<sub>2</sub>O) was added at 2 drops/sec to a 0 °C solution of 46 ml acetic anhydride, (CH<sub>3</sub>CO)<sub>2</sub>O, in 70 ml Et<sub>2</sub>O. Each drop gave a solid material, particularly at the beginning of the reaction, but the precipitate eventually dissolved. After addition was complete, the solution was stirred for 30 minutes at 25 °C and then refluxed for 2 hours. The solution was cooled and then the solvent and the acetic acid byproduct were evaporated to give a very viscous light brown liquid. This material was dissolved in 100 ml of tetrahydrofuran (THF) and slowly added dropwise to 23 g of LiAlH<sub>4</sub> in 100

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ml THF. The heat of reaction maintained a reflux. Each drop produced some bubbling (probably due to reaction with traces of residual acetic acid). After the addition was complete, the mixture was maintained at reflux temperature for one hour longer, until the bubbling stopped. After cooling to 0 °C, the mixture was quenched with 23 ml water, 23 ml of 15% aqueous sodium hydroxide (NaOH), 200 ml hexanes and finally 69 ml water. The mixture was filtered, the solid was washed with 150 ml hexanes, and the combined organic liquids were dried with magnesium sulfate. After several hours, the magnesium sulfate hydrate was filtered off and the solvent was removed in *vacuo*, leaving a colorless liquid. Distillation at 25 mbar pressure gave the major fraction at 109-111 °C, as 11.3 g (65%, based on the diethylenetriamine). NMR confirmed that this product was N,N',N''-triethyldiethylenetriamine (tedeta). Replacing the acetic anhydride in this procedure with propionic anhydride or butyric anhydride or valeric anhydride or hexanoic anhydride gives, respectively, N,N',N''-tripropyl diethylenetriamine (tpdeta), or N,N',N''-tributyl diethylenetriamine (tbdeta), or N,N',N''-triethyl diethylenetriamine (tadeta), or N,N',N''-trihexyl diethylenetriamine (thdeta).

Dialkylethylenediamines were prepared by the following reaction:



Synthesis of N,N'-dihexylethylenediamine (dheda), (CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>NHCH<sub>2</sub>)<sub>2</sub>: In a 20 500-mL flask, ethylenediamine (7.79 mL, 120 mmol) was dissolved in 150 mL of tetrahydrofuran. To this solution, hexanoic anhydride (59.44 mL, 260 mmol) was added dropwise over 40 minutes with vigorous stirring, the solution becoming extremely turbid. The reaction was then refluxed at 78°C for 4 hours. Excess anhydride was quenched by the addition of 0.2 mL of distilled water, and the volatiles, 25 including the byproduct hexanoic acid, were removed *in vacuo*. The resulting solid

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amide was washed into a Buchner funnel (under air) with 2 x 25 mL hexane and pressed dry. In a separate 500-mL flask, lithium aluminum hydride (11.5 g, 300 mmol) was suspended in 150 mL of diethylether and cooled to 0°C. The previously synthesized solid powdered amide was added slowly with evolution of H<sub>2</sub> gas. The rate of addition of amide should be kept low enough so that the generation of foam is controlled. The mixture was then refluxed at 37°C over night. The resulting mixture was then cooled to 0°C and quenched as follows: 1) Water (11.6g, 640 mmol) was added dropwise with vigorous stirring. 2) With the mixture becoming increasingly turbid, a 15% w/w aqueous solution of sodium hydroxide (11.6 g) was added dropwise with vigorous stirring. Hexane was added in amounts sufficient to prevent the mixture from becoming too solid to stir. 3) Water (34.8 g, 1.93 mol) was again added and the mixture became easier to stir. This solution was filtered and the filtrate was stirred with magnesium sulfate over night. This mixture was filtered and the volatiles were removed *in vacuo*, resulting in a clear colorless dihexylethylenediamine (dheda). The dheda was subsequently distilled at 84-90°C at 90 mTorr vacuum (15.5 g, 58% yield). NMR: <sup>1</sup>H in C<sub>6</sub>D<sub>6</sub> (2.62, 4 protons, singlet), (2.52, 4 protons, triplet), 1.42, 4 protons, quintet), (1.26, 12 protons, multiplet), (0.88, 6 protons, triplet).

Replacing the hexanoic anhydride in this procedure with butyric anhydride or valeric anhydride anhydride gives, respectively, N,N'-dibutylethylenediamine (dbeda), (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>NHCH<sub>2</sub>)<sub>2</sub>, or N,N'-diamylethylenediamine (daeda), (CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>NHCH<sub>2</sub>)<sub>2</sub>.

20 A related preferred amine has one methyl group attached to each terminal nitrogen, in addition to the -CH<sub>2</sub>R group. This type of polyamine can be formed from the polyamines just discussed by reductive methylation using formaldehyde and a reducing agent such as formic acid (Clarke-Eschweiler method):



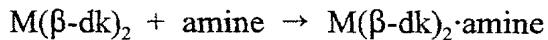
25 Detailed instructions for carrying out this type of reaction have been published by R.

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N. Icke, B. B. Wisegarver and G. A. Alles in *Organic Syntheses, Collective Volume 3*, pages 723-725 (1955). This method is suitable for the synthesis of amines such as N,N'-diethyl-N,N'-dimethylethylenediamine (dedmeda), N,N',N''-triethyl-N,N'-dimethyldiethylenetriamine (tedmdeta), N,N'-dimethyl-N,N',N''-trispropyldiethylenetriamine (dmtpdeta), N,N',N''-tributyl-N,N'-dimethyldiethylenetriamine (tbdmdeta), N,N',N''-triethyl-N,N'-dimethyldiethylenetriamine (tadmdeta), and N,N',N''-trihexyl-N,N'-dimethyldiethylenetriamine (thdmdeta).

6. Synthesis and Use of Amine-Complexed Alkaline Earth Metal Beta-Diketonates

The novel amine-complexed metal beta-diketonates of this invention may be formed simply by reacting a suitable amine with an alkaline earth metal beta-diketonate ( $M(\beta\text{-dk})_2$ ).



The liquid amine and product act as solvent for the reaction. If the amine adduct is solid, a small amount of added solvent is necessary to facilitate the reaction.

Alternatively, the reaction forming the alkaline earth metal beta-diketonate may be carried out in the presence of the amine.

Beta-diketonates of the larger alkaline earth metals, barium and strontium, may accommodate amines with up to four nitrogens coordinated to the metal, while smaller calcium usually binds no more than three nitrogens, and magnesium usually no more than two nitrogens.

The novel amine-complexed metal beta-diketonates of this invention are generally liquids at room temperature. The vapor of these liquids may be formed in a thin-film evaporator, or by nebulization into a carrier gas preheated to about 250 °C. The nebulization may be carried out pneumatically or ultrasonically. The amine-complexed alkaline earth liquid metal beta-diketonates are generally completely miscible with organic solvents, including hydrocarbons, such as dodecane, tetradecane, xylene and mesitylene, and with alcohols, ethers, esters, ketones and

chlorinated hydrocarbons. These solutions generally have lower viscosities than the pure liquids, so that in some cases it may be preferable to nebulize and evaporate the solutions rather than the pure liquids. Those amine-complexed metal beta-diketonates that are solid at room temperature are generally extremely soluble in organic solvents.

5 Such solutions can also be evaporated with thin-film evaporators or by nebulization.

Thin-film evaporators are made by Artisan Industries (Waltham, Massachusetts).

Commercial equipment for direct vaporization of liquids (DLI) is made by MKS Instruments (Andover, Massachusetts), Advanced Technology Materials,

Inc. (Danbury, Connecticut), Novellus Systems, Inc. (San Jose, California) and COVA

10 Technologies (Tiburon, California). Ultrasonic nebulizers are made by Sonotek

Corporation (Milton, New York) and Cetac Technologies (Omaha, Nebraska).

The process of the invention can be carried out in standard equipment well known in the art of chemical vapor deposition (CVD). The CVD apparatus brings the vapors of the reactants into contact with a heated substrate on which the material deposits. A CVD process can operate at a variety of pressures, including in particular normal atmospheric pressure, and also lower pressures. Commercial atmospheric pressure CVD furnaces are made in the USA by the Watkins-Johnson Company

(Scotts Valley, California), BTU International (North Billerica, Massachusetts) and

SierraTherm (Watsonville, California). Commercial atmospheric pressure CVD

20 equipment for coating glass on the float production line is made in the USA by

Pilkington-Libbey-Owens-Ford Company (Toledo, Ohio), PPG Industries (Pittsburgh,

Pennsylvania) and AFG Industries (Kingsport, Tennessee). Low-pressure CVD

equipment is made by Applied Materials (Santa Clara, California), Spire Corporation

(Bedford, Massachusetts), Materials Research Corporation (Gilbert, Arizona),

25 Novellus Systems, Inc. (San Jose, California), Emcore Corporation (Somerset, NJ) and

NZ Applied Technologies (Woburn, Massachusetts).

The liquids and solutions described herein may also be used as metal-containing precursors for other types of deposition processes, such as spray coating, spin coating or sol-gel formation of mixed metal oxides. The high solubility and

miscibility of these precursors is an advantage in forming the required solutions.

#### EXAMPLE 1

A liquid compound was prepared by reacting equal molar amounts of Ba(thd)<sub>2</sub> and N,N',N''-trihexyldiethylenetriamine (thdeta) in hexane until all the solid dissolved, and then removing the hexane by warming the solution under reduced pressure. A viscous light yellow liquid remained. The compound is monomeric by cryoscopy. The viscosity of this liquid compound can be reduced, for easier handling and vaporization, by dissolving it in a high-boiling solvent, such as additional N,N',N''-trihexyldiethylenetriamine (thdeta) or a hydrocarbon such as mesitylene. Ultrasonic nebulization of such a solution and passage through a tube furnace at 250 °C resulted in complete evaporation of the fog droplets, demonstrating its utility as a vapor source.

#### EXAMPLES 2-9

Similar procedures were used to form and volatilize the liquid compounds between the barium beta-diketonates and the amines shown in Table 3.

Table 3. Liquid Amine Complexes of Barium Beta-Diketonates

Exempl e	$\beta$ - diketonates(t)	Amine (t)	Total #var	Viscosity centipoise	Molecular Complexity
					1
1	td(4)	thdeta(15)	19	1861	0.93
2	td(4)	thdmelta(15)	19		
3	td(4)	tadeta(12)	16	3845	0.94
4	td(4)	tadmelta(12)	16		
5	thd(0)	thdeta(15)	15	3292	1.03
6	td(4)	tbdelta(9)	13		
7	thd(0)	tadeta(12)	12	6782	1.02
8	thd(0)	tbdelta(9)	9	$>10^4$	
9	td(4)	tedeta(3)	7	$>10^4$	

As shown in Table 3, all these liquid compounds of barium beta-diketonates and amines have 7 or more angular variables. The liquids with the lowest viscosities all have 15 or more angular variables. Those with less than 10 angular variables have very high viscosities. Molecular weights were measured by cryoscopy in p-xylene

solution for four of the compounds, resulting in values close to the values expected for monmers ("molecular complexity" near unity).

#### EXAMPLES 10-17

Other combinations of barium beta-diketonates and amines were found to be solids at room temperature, with low melting points, typically less than 100 °C, and more preferably below 60 °C. They are highly soluble in organic solvents, so that their concentrated solutions can be used in liquid injection systems. Typical preferred concentrations are greater than 1 molar, while lower concentrations, such as 0.5 molar, yield solutions with lower viscosity. Table 4 lists some of these highly soluble solid compounds of barium beta-diketonates and amines.

Table 4. Examples of Low Melting Highly Soluble Solid Barium Beta-Diketonate-Amine Compounds.

Exempl e	β- diketones(t)	Amine(t)	Total	Melting Point (°C)
			#var	
10	tod(4)	tpdeta(6)	10	
11	tod(4)	dmtpdeta(6)	10	38-43
12	tod(4)	pedeta(5)	9	
13	tod(4)	tedmdeta(3)	7	48-54
14	thd(0)	tpdeta(6)	6	
15	thd(0)	dmtpdeta(6)	6	
16	thd(0)	pedeta(5)	5	
17	thd(0)	tedeta(3)	3	

As shown in Table 4, all these examples of low-melting, highly soluble solids have between 3 and 10 additional angular variables.

#### EXAMPLE 18

Synthesis of Sr(tod)<sub>2</sub>: Metallic strontium (1.82 g, 21 mmol) and 2,2,6,6-tetramethyloctane-3,5-dione (Htod) (8.23 g, 42 mmol) were mixed in a flask; gas started bubbling from the metal's surface. To this, 75 mL of tetrahydrofuran (thf) was added and NH<sub>3</sub> gas was bubbled into the solution *via* syringe for 1 minute. The reaction became very vigorous and was allowed to stir for 2 hours, with periodic

-25-

charging of the solution with  $\text{NH}_3$  to maintain the metal activation. The  $\text{NH}_3$  was removed *in vacuo* and the solution was filtered to remove a small amount of suspended powder. The volatiles were removed *in vacuo*, leaving a waxy white solid. This solid was pumped at 60°C for 3 hours to completely remove thf from the  $\text{Sr}(\text{tod})_2$  (6.5 g, 65% yield).  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ): (5.57 ppm, 1 proton, broad singlet), (1.42 ppm, 2 protons, quartet), (1.05 ppm, 9 protons, singlet), (1.01 ppm, 6 protons, singlet), (0.72 ppm, 3 protons, triplet)

Synthesis of  $\text{Sr}(\text{tod})_2\cdot\text{thdeta}$ : In a 10-mL flask,  $\text{Sr}(\text{tod})_2$  (1.16 g, 2.4 mmol) and  $\text{N,N}',\text{N}''\text{-trihexyldiethylenetriamine}$  (0.849 g, 2.4 mmol) were mixed in 5 mL of benzene. The solution was stirred for a few minutes until the solid dissolved. The resulting solution of  $\text{Sr}(\text{tod})_2\cdot\text{thdeta}$  was stirred under vacuum at 50°C for 3 hours to remove the benzene. The resulting liquid had a viscosity of 489 centipoise at 40 °C. Ultrasonic nebulization of the liquid and passage through a tube furnace at 250 °C resulted in complete evaporation of the fog droplets, demonstrating its utility as a vapor source.

#### EXAMPLES 19-22

The strontium beta-diketonates in the Table 5 were synthesized in a similar manner to that described in Example 18.

Table 5. Liquid Amine Complexes of Strontium Beta-Diketonates

Example	$\beta$ -diketone(t)	Amine(t)	Total	Viscosity	Molecular
				#var	centipoise Complexity
18	tod(4)	thdeta(15)	19	489	0.89
19	tod(4)	tadeta(12)	16	638	0.83
20	thd(0)	thdeta(15)	15	1030	1.01
21	thd(0)	tadeta(12)	12	2008	0.99
22	tod(4)	tedeta(3)	7	$>10^4$	0.94

The viscosities decrease with increasing numbers (listed in the #var column of Table 5) of C-C single bonds that rotate alkyl groups with less symmetry than a methyl or a

tert-butyl group. For the strontium compounds, the lowest viscosities are found for compounds with 12 or more angular variables.

After several weeks at room temperature, one batch (out of four) of  $\text{Sr}(\text{thd})_2\cdot\text{tadeta}$  partially crystallized. An X-ray analysis of a crystal showed three inequivalent monomeric molecules, one of which is depicted in Figure 1. The other two molecular units show a similar 7-coordinate strontium center, but differ in the torsion angles of the three pentyl chains attached to the three nitrogens. Cryoscopy showed that the amine-complexed materials are also monomeric in p-xylene solution. This structure is in contrast with the trimeric nature of  $\text{Sr}(\text{thd})_2$  in its crystalline solid without any amine ligand, as determined by E. Berg and N.M. Herrera, *Anal. Chim. Acta*, vol. 60, p. 117, (1972); S. R. Drake, M. B. Hursthouse, K. M. A. Malik and D. J. Otway, *J. Chem. Soc., Dalton Trans.* 1993, p. 2883.

All the strontium compounds in Table 5 were successfully flash vaporized.

#### EXAMPLES 23-26

The liquid calcium compounds listed in Table 6 were prepared. The following procedure is typical:

Synthesis of  $\text{Ca}(\text{thd})_2$ : In a 100-mL round bottom, Ca shot (0.54 g, 13.5 mmol), 2,2,6,6,-tetramethylheptane-3,5-dione (Hthd) (5.0 g, 27.1 mmol) and ethanol (2.50 g, 54.3 mmol) were combined in 30 mL of tetrahydrofuran (thf) and refluxed over night. A very small amount of dark suspended powder was filtered off. The volatiles were removed *in vacuo* from the clear filtrate. The white solid was then dried at 50°C for 3 hours under vacuum, resulting in 4.43 g of  $\text{Ca}(\text{thd})_2$  (86% yield).  $^1\text{H}$  NMR (in  $d_5$ -pyridine): (5.92 ppm, 1 proton, singlet), (1.23 ppm, 18 protons, singlet)

Synthesis of  $\text{Ca}(\text{thd})_2\cdot\text{dheda}$ : In a 5-dram vial,  $\text{Ca}(\text{thd})_2$  (1.00g, 2.4 mmol) was combined with N,N'-dihexylethylenediamine (dheda) (0.56 g, 2.4 mmol) and heated to 45°C. Clear, liquid  $\text{Ca}(\text{thd})_2\cdot\text{dheda}$  formed quantitatively.  $^1\text{H}$  NMR (in  $d_5$ -pyridine): (5.91 ppm, 2 protons, singlet), (2.77 ppm, 4 protons, multiplet), (2.64 ppm, 4 protons, quartet), (1.68 ppm, 2 protons, multiplet), (1.51 ppm, 4 protons, quintet), (1.23 ppm, 36 protons, singlet), 1.1-1.4 ppm, 6 protons, broad multiplet), (0.83 ppm, 6

protons, triplet).

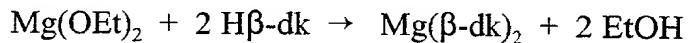
Table 6. Liquid Amine Complexes of Calcium Beta-Diketonates

Example	$\beta$ -diketones	Amine	#var	Viscosity	Molecular
				centipoise	Complexity
23	tod(4)	thdeta(15)	19	214	0.85
24	3hd(2)	thdeta(15)	17	78	1.02
25	thd(0)	thdeta(15)	15	270	1.03
26	3hd(2)	dheda(10)	12	135	0.93

All the calcium compounds in Table 6 were successfully flash vaporized.

#### EXAMPLES 27-31

The liquid magnesium compounds listed in Table 7 were prepared. The magnesium  $\beta$ -diketonates were formed by the reaction of magnesium ethoxide with the appropriate H  $\beta$ -diketone:



Synthesis of  $\text{Mg}(\text{thd})_2$ : In a 100-mL round bottom,  $\text{Mg(OEt)}_2$  was suspended in dimethoxyethane (DME) and a DME solution of 2,2,6,6-tetramethylheptane-3,5-dione (Hthd) was added by cannula. The solution was refluxed at 90°C overnight. The resulting cloudy solution was reduced to a solid *in vacuo* and taken up in 50 mL of tetrahydrofuran (thf). A small amount of solid was filtered off and the volatiles were again removed leaving 5.6 g of white  $\text{Mg}(\text{thd})_2$  (82% yield).  $^1\text{H}$  NMR (in  $d_5$ -pyridine): (5.75 ppm, 1 proton, singlet), (1.23 ppm, 18 protons, singlet)

Synthesis of  $\text{Mg}(\text{thd})_2\text{-dheda}$ : In a 10-mL flask,  $\text{Mg}(\text{thd})_2$  (3.80 g, 97.0 mmol) and theda (2.22 g, 97.0 mmol) were mixed without solvent. After slight warming, clear, slightly yellow liquid  $\text{Mg}(\text{thd})_2\text{-dheda}$  was formed. This material was distilled at 72°C at 27 mTorr (4.03g, 67% yield). NMR:  $^1\text{H}$  in  $\text{C}_6\text{D}_6$  (5.76, 2 protons, singlet), (2.58 ppm, 4 protons, broad singlet), (2.41 ppm, 4 protons, broad multiplet), (1.46 ppm, broad singlet, 2 protons), (1.40-1.10 ppm, 16 protons, broad multiplets buried

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under a singlet), (1.26 ppm, 18 protons, singlet), (0.90 ppm, 6 protons, triplet).

Table 7. Liquid Amine Complexes of Magnesium Beta-Diketonates

Example	$\beta$ -diketone	Amine	#var	Viscosity centipoise	Molecular Complexity	Vapor P. °C/mtorr
27	tod(4)	dheda(10)	14	110	1.03	158/27
28	3hd(2)	dheda(10)	12	48	1.13	123/31
29	thd(0)	dheda(10)	10	113	0.89	72/27
30	tod(4)	dbeta(6)	10	381	0.94	
31	3hd(2)	dbeda(6)	8	54	0.95	

Low viscosities were found for magnesium compounds with as few as 8 angular variables. All the magnesium compounds in Table 7 could be flash vaporized, and the three listed with vapor pressures were successfully vacuum distilled under the conditions given.

### EXAMPLE 32

Ba(thd)<sub>2</sub>·thdeta from Example 1 was nebulized through a Sonotek ultrasonic nozzle projecting into a stream of nitrogen gas preheated to 250 °C and 80 Torr pressure. The fog droplets evaporated, forming a transparent vapor mixture. The vapor mixture was passed into a tube furnace at 450 °C. A film on barium carbonate, BaCO<sub>3</sub>, deposited on the inner walls of the tube furnace and on silicon substrates placed within the heated zone of the furnace.

### EXAMPLE 33

Titanium bis(n-butoxide) bis(tod) was formed by reaction of titanium n-butoxide with a Htod. 5.78 g (0.017 mol) of titanium n-butoxide was placed in a glass reaction flask and 15 ml hexanes were added. 6.74 g (0.034 mol) of Htod was added and stirred for 10 min, and the hexane solvent was removed in vacuum. The reaction mixture was heated to 80 °C under vacuum until no more bubbling occurred, in order to remove the byproduct n-butanol. 9.65 g (97%) of a clear, pale yellow liquid titanium bis(n-butoxide) bis(tod) product was recovered.

Equal molar quantities of Ba(thd)<sub>2</sub>·thdeta from Example 1 and the titanium bis(n-butoxide) bis(tod) were mixed together. This liquid mixture was pumped at a 0.10 cc/min

liquid flow rate into an ultrasonic nebulizer, through which nitrogen gas at 80 Torr pressure and 400 standard cc/min was passed. The resulting fog was mixed with a dry air flowing at 200 standard cc/min, and this combined mixture flowed at a pressure of 80 Torr into a tubular reactor (25 mm inside diameter) heated inside a tube furnace at 500 °C. A transparent coating was formed on glass and silicon substrates in the tube furnace, as well as on the inside wall of the tube. The film was determined to be barium titanate, BaTiO<sub>3</sub>, by RBS, along with some carbon contamination. The carbon was removed by annealing for 10 minutes at 600 °C in flowing oxygen gas.

#### EXAMPLE 34

The precursors for barium from Example 1, strontium from Example 18 and titanium from Example 33 were mixed in the molar ratio 7:3:10 and used in a CVD experiment similar to Example 33, with a substrate temperature 500 °C. The resulting barium strontium titanate film contained some carbon contamination, which was removed by annealing for 10 minutes at 600 °C in flowing oxygen gas.

#### EXAMPLES 35-39

Some additional examples of liquid barium compounds were prepared. These examples have even lower viscosities than the other barium compounds listed in Tables 3 and 4. The viscosities of the barium compounds based on the 2,2,6-trimethylheptane-3,5-dione (H3hd) ligand are particularly low, making these liquids easy to handle.

Table 8. Additional Examples of Liquid Barium Compounds

Example	β-diketones(t)	Amine(t)	Total #var	Viscosity centipoise	Molecular Complexity
35	3hd(2)	thteta (20)	22	246	0.85
36	3hd(2)	thdeta(15)	17	455	0.93
37	3hd(2)	tadeta(12)	14	811	1.00
38	thd(0)	thteta (20)	20	1223	0.97
39	tod(4)	thteta (20)	24	1236	0.90

The liquid precursors of the present invention may be combined with bismuth and tantalum precursors to provide a process for depositing strontium bismuth tantalate films having ferroelectric properties. Similarly, by combining an iron-containing precursor with

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the precursors of this invention, barium ferrites having magnetic properties may be formed.

The liquids and solutions disclosed in these examples all appeared to be non-pyrophoric by the methods published by the United States Department of Transportation.

5 One test calls for placing about 5 milliliters of the liquid or solution on an non-flammable porous solid, and observing that no spontaneous combustion occurs. Another test involves dropping 0.5 milliliters of the liquid or solution on a Whatman No. 3 filter paper, and observing that no flame or charring of the paper occurs.

The precursors generally react slowly with the moisture in ambient air, and should be stored under a dry atmosphere such as nitrogen.

Those skilled in the art will recognize or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described specifically herein. Such equivalents are intended to be encompassed in the scope of the following claims.

15 What is claimed is:

1. A composition of matter for use in the formation of alkaline earth-containing materials, comprising:

5 a compound comprising an alkaline earth metal beta-diketonate (and the isoelectronic derivatives thereof) and an amine, said compound being a liquid at 60 °C and capable of being vaporized.

10 2. A composition of matter for use in the formation of alkaline earth-containing materials, comprising:

15 a compound comprising an alkaline earth metal beta-diketonate (and the isoelectronic derivatives thereof) and an amine, said compound being a liquid at 20 °C and capable of being vaporized.

20 3. The composition of matter as in claim 1, wherein the beta-diketonate has the formula,  $^1\text{RC}(=\text{O})\text{CHR}^3\text{C}(=\text{O})\text{R}^2$ , where  $^1\text{R}$  and  $\text{R}^2$  are independently selected and are an alkyl group, a fluoroalkyl group, an alkyl group substituted by other elements, or an aryl group; and  $\text{R}^3$  may be hydrogen, an alkyl group, a fluoroalkyl group, or an alkyl group substituted by other elements.

25 4. The composition of claim 3, wherein the groups  $^1\text{R}$  and  $\text{R}^2$  contain four or five carbons.

5. The composition of claim 3, wherein the group  $\text{R}^3$  contains less than two carbons.

25 6. The composition of claims 4 or 5, wherein the beta-diketonate ligand is chosen from those listed in Table 1 of the specification.

7. The composition of matter as in claim 1 or 2, wherein the amine has the formula,  $\text{R}^a\text{N}(\text{R}^b)\text{CH}_2\text{CH}_2\{\text{N}(\text{R}^c)\text{CH}_2\text{CH}_2\}_n\text{N}(\text{R}^d)\text{R}^e$ , wherein  $\text{R}^a$ ,  $\text{R}^b$ ,  $\text{R}^c$ ,  $\text{R}^d$ , and  $\text{R}^e$  are

independently selected and are hydrogen or an alkyl group, a fluoroalkyl group, an alkyl group containing oxygen- or nitrogen-containing species or an aryl group, and n is a non-negative integer.

5 8. The composition of matter as in claim 7, wherein n has the value 0, 1 or 2.

9. The composition of matter as in claim 7, wherein n has the value 1.

10. The composition of matter as in claim 7, wherein at least one of the groups R<sup>a</sup>, R<sup>b</sup>, R<sup>c</sup>, R<sup>d</sup>, and R<sup>e</sup> contains more than one carbon atom.

11. The composition of matter as in claim 7, wherein the amine is selected from Table 2 of the specification.

12. The composition of matter as in claim 1, wherein the amine complex of a barium beta-diketonate is chosen from Table 4 of the specification.

13. The composition of matter as in claim 2, wherein the compound is chosen from Tables 3, 5, 6, 7 or 8 of the specification.

20 14. The composition of matter as in claim 1, wherein the compound has a solubility greater than 1 molar in a liquid solvent.

25 15. The composition of matter as in claim 1, wherein the compound has a solubility greater than 0.5 molar in a liquid solvent.

16. A process for forming a material containing an alkaline-earth metal, comprising:

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providing a liquid comprising a compound including an alkaline earth metal beta-diketonate (and the isoelectronic derivatives thereof) and an amine, and

contacting the liquid or its vapor with a heated surface in a deposition process to deposit a material containing an alkaline-earth metal.

5

17. The process of claim 16 in which the deposited material comprises one or more metal oxides.

18. The process of claim 16 in which the metal or metals are selected from the group consisting of barium, strontium and titanium.

19. The process of claim 16 in which the metal or metals are selected from the group consisting of strontium, bismuth, niobium and tantalum.

15. The process of claim 16, wherein a sol-gel process is used to deposit material containing one or more metals or metal oxides.

21. The process of claim 16, wherein a spray-coating or spin-coating process is used to deposit material containing one or more metals or metal oxides.

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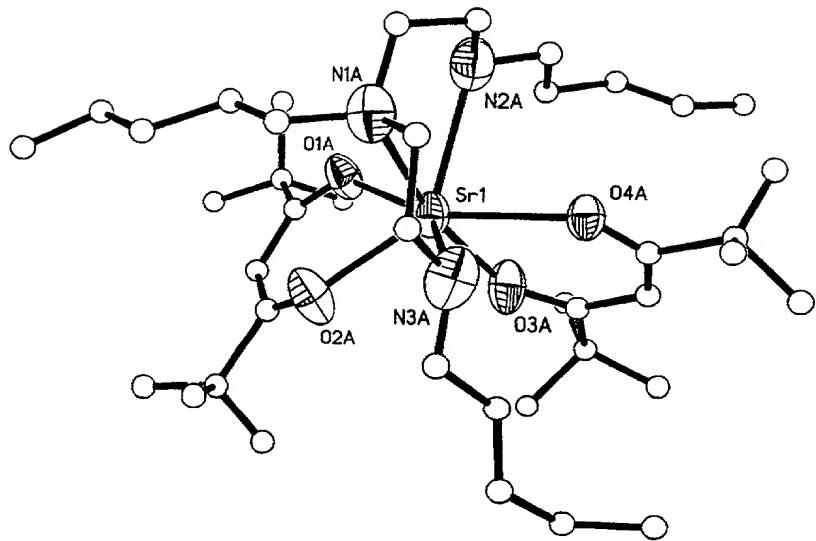


FIG. 1

**DECLARATION AND POWER OF ATTORNEY**  
**(Attorney Docket No. 42697.124)**

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship is as stated below next to my name.

I believe that I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

**LIQUID COMPOUNDS FOR FORMATION OF MATERIALS CONTAINING ALKALINE EARTH METALS**

the specification of which (check only one):

is attached hereto.

was filed as United States Patent Application  
 Serial No. \_\_\_\_\_  
 on \_\_\_\_\_  
 and was amended  
 on \_\_\_\_\_  
 (if applicable)

was filed as PCT Patent Application  
 Serial No. PCT/US99/24533  
 on October 20, 1999  
 and was amended under PCT Article 19  
 on \_\_\_\_\_  
 (if applicable)

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the patentability of the claims of this application in accordance with Title 37, Code of Federal Regulations, Sections 1.56(a) and 1.56(b).

I hereby claim foreign priority benefits under Title 35, United States Code, §119(a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS  
UNDER 35 U.S.C. §119(s)-(d) or 365(b):

COUNTRY (If PCT indicate PCT)	APPLICATION NUMBER	DATE OF FILING	PRIORITY CLAIMED UNDER 35 U.S.C. §119(a)- (b) or 365(b) (YES/NO)
			NO

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional patent application(s) listed below:

APPLICATION NUMBER	DATE OF FILING	STATUS: (PENDING OR ABANDONED)
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I hereby claim the benefit under Title 35, United States Code, § 120 or 365(c) of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, § 112. I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56 which occurred between the filing date of the prior applications and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATION OR PCT INTERNATIONAL APPLICATION(S)  
DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. § 120 or 365(c):

APPLICATION NUMBER	DATE OF FILING (day, month, year)	STATUS: (PATENTED, PENDING OR ABANDONED)
60/105,158	21 October 1998	Abandoned
60/126,793	30 March 1999	Abandoned

POWER OF ATTORNEY: As named inventors, we hereby appoint the following attorneys and/or agents to prosecute this application and transact all business in the Patent and Trademark Office connected therewith

44

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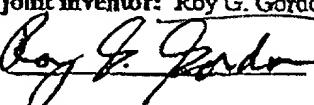
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Wherefore I petition that letters patent be granted to me for the invention or discovery described and claimed in the attached specification and claims, and hereby subscribe my name to said specification and claims and to the foregoing declaration, power of attorney, and this petition.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements

were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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